Adsorption of Carbon Dioxide on Amine-modified MSU-H Silica in the Presence of Water Vapor

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Mesoporous MSU-H silica modified with 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane showed high capacity of 3.08 mmol·g^{-1} for carbon dioxide adsorption under 15 kPa of carbon dioxide and 12 kPa of water vapor at 333 K.

Increased atmospheric concentration of carbon dioxide (CO_2) is a serious environmental problem. Carbon dioxide capture and storage (CCS) can reduce CO_2 emissions to the atmosphere.[1] Separation of CO_2 emitted from large point sources, e.g., power plants, is the first step of CCS. Of the total costs of CCS, 70–80% are energy costs of CO_2 separation from flue gases.[1] The usual means of large-scale CO_2 separation, absorption using aqueous amine solution, is energy intensive; to regenerate the absorbent, the temperature of a large volume of aqueous solution must be changed. Moreover, corrosion of equipment also occurs. Recently, amine-grafted mesoporous silicas have been proposed as CO_2 adsorbents.[2] They can overcome such obstacles to absorption processes. Furthermore, amine-grafted mesoporous silicas have an advantage over traditional adsorbents such as activated carbon and zeolites because they can adsorb CO_2 in the presence of water vapor,[2] which is usually present in flue gases from fossil fuel combustion. The issue of amine-grafted mesoporous silicas is their poor adsorption capacity because of limited amine loading and low amine efficiency. Herein, we report that amine-modified MSU-H silica provides high CO_2 adsorption capacity and high stability for recycle use in the presence of water vapor.

The MSU-H silica was prepared using a method similar to that reported by Kim et al.[3] (see ESI).[4] The TEM images of the MSU-H silica used show that it has a hexagonal structure with ca. 10-nm pore diameter; however, the sizes of periodic domains that compose aggregates are small (<100 nm) (Figure S1).[4] Two adsorbents were prepared by modification of MSU-H with triamine, 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (TA). A TA/MSU-H(I) adsorbent was prepared by grafting of TA as reported previously.[2e] A TA/MSU-H(II) adsorbent was prepared by further impregnation of the TA/MSU-H(I) adsorbent (1.96 g) with ethanol solution of TA (67 wt %, 1.18 g) and subsequent drying overnight at 333 K in air.

Nitrogen (N_2) adsorption–desorption isotherms of the samples were measured at 77 K, and surface areas and pore size distributions were calculated. The BJH pore size distributions showed that uniform mesopores were present for TA/MSU-H(I); the pore size of which (7.4 nm) was less than that of MSU-H (9.0 nm), reflecting that the pore surface was modified with TA for TA/MSU-H(I) (Figure S2).[4] In contrast, no peak was observed in the pore size distribution of TA/MSU-H(II), reflecting that most mesopores were filled with condensed TA for TA/MSU-H(II). The TA molecules would be condensed to each other in the mesopores of MSU-H for TA/MSU-H(II).[2d] The surface area decreased with increased amine content (Table 1). Although mesopores of TA/MSU-H(II) were filled, the surface area of TA/MSU-H(II) was high (45 m^2·g^{-1}) as a result of high external surface area of the MSU-H silica. Another adsorbent (TA/SBA-15(II)) using SBA-15 mesoporous silica as support was prepared for comparison; its amine content (7.0 mmol·g^{-1}) was similar to that of TA/MSU-H(II), and its mesopores were also filled with condensed TA. The surface area of TA/SBA-15(II) (4 m^2·g^{-1}) was much lower than that of TA/MSU-H(II), which would result from low external surface area of the SBA-15 silica due to larger sizes of periodic domains (≈1000 nm, Figure S3).[4]

Table 1. Physicochemical properties of samples

Sample	Surface area[a] /m^2·g^{-1}	Amine content[b] /mmol·g^{-1}
MSU-H	543	—
TA/MSU-H(I)	198	5.15
TA/MSU-H(II)	45	7.47
TA/SBA-15(II)	4	7.00

[a]Surface area calculated by the BET method. [b]Nitrogen atom amounts determined by elemental analysis.

The CO_2 adsorption capacities were examined under a condition (CO_2 and water vapor pressure, and temperature) similar to that of flue gases from coal-fired power plants. The capacities of TA/MSU-H(I) and TA/MSU-H(II) in the presence of water vapor are listed in Table 2 along with those of TA/SBA-15(II) and TA-grafted SBA-15 (TA/SBA-15).[2e] The adsorption capacity of TA/MSU-H(II) was found to be the highest in the presence of water vapor, indicating that filling of mesopores of MSU-H with condensed TA is effective to improve the adsorption capacity in the presence of water vapor. Moreover, TA/MSU-H(II) showed higher amine efficiency than TA/MSU-H(I). More than 80% of nitrogen atoms on TA/MSU-H(II) are thought to be involved in the CO_2 adsorption because TA reacts with CO_2 to form carbamate in the presence of water vapor.[2e] It is suggested that the configuration of condensed TA in the mesopores of MSU-H is suitable for carbamate formation. In contrast, pore filling with condensed TA was not effective for SBA-15. The adsorption capacity and the amine efficiency of TA/SBA-15(II) were much lower than those of TA/SBA-15, which would be because of low surface area of TA/SBA-15(II).

Water vapor enhanced the CO_2 adsorption on TA/MSU-H(II) and TA/SBA-15(II) whose mesopores were filled with condensed TA. However, the influence of water vapor was

Table 2. Capacity of various adsorbents for CO_2 adsorption

Adsorbent	Adsorption capacity /mmol·g^{-1}	Amine efficiency[a]	Ref
TA/MSU-H(I)	1.80[b]	0.35	Present work
TA/MSU-H(II)	3.08[b]	0.41	Present work
TA/SBA-15	1.80[b]	0.31	2e
TA/SBA-15(II)	1.77[b]	0.25	Present work
TA/HMS	0.95[c]	0.25	2h
TA/PE-MCM-41[d]	2.94[e]	0.37	2i
Zeolite 13X	3.18[f]	—	Present work

[a] (CO_2 adsorbed (mol))/(nitrogen atoms in adsorbent (mol)). [b] 15 kPa of CO_2, 12 kPa of water vapor, and 74 kPa of N_2 at 333 K. [c] 90 kPa of CO_2, 0.71 kPa of water vapor, and 10 kPa of argon at 293 K. [d] PE-MCM-41: pore-expanded MCM-41. [e] 5 kPa of CO_2, 0.85 kPa of water vapor, and 95 kPa of N_2 at 298 K. [f] 15 kPa of CO_2 and 86 kPa of N_2 at 333 K.

smaller for TA/MSU-H(II) than for TA/SBA-15(II). In the absence of water vapor, TA/MSU-H(II) adsorbed 2.24 mmol·g^{-1} of CO_2 (27% lower than its adsorption capacity in the presence of water vapor), whereas TA/SBA-15(II) adsorbed only 0.46 mmol·g^{-1} (74% lower). We have reported that amine-grafted mesoporous silica, whose anchored aminosilane molecules are exposed to the surface, exhibits comparable adsorption capacity in the absence and presence of water vapor, whereas aminosilane gel (having low surface area of ≈ 2 m^2·g^{-1}) prepared by the condensation of aminosilane molecules can adsorb CO_2 only in the presence of water vapor.[2d] Water vapor would swell the aminosilane gel and/or hydrolyze siloxane bonds of the aminosilane gel, which would enable the interior amino groups of the gel to react with CO_2. Smaller influence of water vapor on the adsorption capacity of TA/MSU-H(II) than that of TA/SBA-15(II) suggests that the interior amino groups of TA/MSU-H(II) exist nearer to the surface than those of TA/SBA-15(II) because of higher surface area of TA/MSU-H(II) and can more easily react with CO_2, which explains the higher adsorption capacity and amine efficiency of TA/MSU-H(II).

It has been reported that TA-grafted mesoporous silicas exhibit the highest CO_2 adsorption capacity among various amine-grafted mesoporous silicas.[2] Data form relevant studies in the literature for the CO_2 adsorption capacity of TA-grafted mesoporous silicas are also listed in Table 2.[2h,2i] The CO_2 adsorption capacity of TA/MSU-H(II) was higher than those of TA-grafted mesoporous silicas, but adsorption conditions were different. Additionally, we compared the adsorption capacity of TA/MSU-H(II) with that of zeolite 13X, which is a traditional adsorbent having the largest adsorption capacity in the absence of water vapor.[4] The capacity of TA/MSU-H(II) in the presence of water vapor was comparable to that of zeolite 13X under identical conditions, except for the absence of water vapor (Table 2).

Figure 1A shows breakthrough curves of CO_2 over TA/MSU-H(II) and TA/SBA-15(II) in the presence of water vapor and over zeolite 13X in the absence of water vapor. Outlet CO_2 concentration increased rapidly after 20 min for TA/MSU-H(II). The shape of the breakthrough curve over TA/MSU-H(II) resembled that over zeolite 13X, suggesting that the rate of CO_2 adsorption on TA/MSU-H(II) resembles that on zeolite 13X. In contrast, the outlet CO_2 concentration increased gradually for TA/SBA-15(II), indicating that the adsorption rate of TA/SBA-15(II) is lower than that of TA/SBA-15(II). The higher surface area of TA/MSU-H(II) could be responsible for higher CO_2 adsorption rate of TA/MSU-H(II).

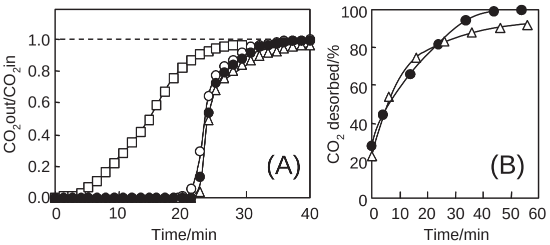

Figure 1. (A) Breakthrough curves of CO_2 for TA/SBA-15(II) (□), fresh TA/MSU-H(II) (●), and TA/MSU-H(II) after 30 cycles of adsorption (333 K)–desorption (393 K) (○) under 15 kPa of CO_2, 12 kPa of water vapor and 74 kPa of N_2 at 333 K, and that for Zeolite 13X (△) under 15 kPa of CO_2 and 86 kPa of N_2 at 333 K. Total flow rate, 30 cm^3·min^{-1}; weight of adsorbent, 1.5 g. (B) Desorption of CO_2 in a helium flow (30 cm^3·min^{-1}) form TA/MSU-H(II) at 393 K (●), and that from Zeolite 13X at 373 K (△). Adsorption conditions were same as those of Figure 1A.

The CO_2 desorption behavior of TA/MSU-H(II) was also examined in a helium flow after adsorption at 333 K (Figure 1B). By heating from 333 to 393 K at a rate of 10 K·min^{-1}, 27% of adsorbed CO_2 was desorbed; then CO_2 was desorbed completely at 393 K in 45 min. Similar desorption behavior of zeolite 13X was observed at a lower temperature (373 K) (Figure 1B), because of stronger adsorption of CO_2 on TA/MSU-H(II) than on zeolite 13X, which explains the water tolerance of TA/MSU-H(II). We also verified the adsorption performance of TA/MSU-H(II) after 30 cycles of adsorption at 333 K and desorption at 393 K.[4] The adsorption capacity after 30 cycles was 2.98 mmol·g^{-1}, only slightly lower (3.2%) than the initial adsorption capacity. Also, the breakthrough curve after 30 cycles resembled the initial one (Figure 1A), suggesting that the rate of adsorption is unchanged. These results show that amine-modified MSU-H silica, with condensed TA filling its pores, is stable during the adsorption–desorption cycles and can be useful for practical applications.

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References and Notes

1 *IPCC Special Report on Carbon Dioxide Capture and Storage*, ed. by B. Metz, O. Davidson, H. de Coninck, M. Loos, L. Meyer, Cambridge University Press, Cambridge, **2005**.

2 a) A. C. C. Chang, S. S. C. Chuang, M. Gray, Y. Soong, *Enagy Fuels* **2003**, *17*, 468. b) H. Y. Huang, R. T. Yang, D. Chinn, C. L. Munson, *Ind. Eng. Chem. Res.* **2003**, *42*, 2427. c) N. Hiyoshi, K. Yogo, T. Yashima, *Chem. Lett.* **2004**, *33*, 510. d) N. Hiyoshi, K. Yogo, T. Yashima, *J. Jpn. Petrol. Inst.* **2005**, *48*, 29. e) N. Hiyoshi, K. Yogo, T. Yashima, *Microporous Mesoporous Mater.* **2005**, *84*, 357. f) S. Kim, J. Ida, V. V. Guliants, J. Y. S. Lin, *J. Phys. Chem. B* **2005**, *109*, 6287. g) F. Zheng, D. N. Tran, B. J. Busche, G. E. Fryxell, R. S. Addleman, T. S. Zemanian, C. L. Aardahl, *Ind. Eng. Chem. Res.* **2005**, *44*, 3099. h) G. P. Knowles, S. W. Delaney, A. L. Chaffee, *Ind. Eng. Chem. Res.* **2006**, *45*, 2626. i) P. J. E. Harlick, A. Sayari, *Ind. Eng. Chem. Res.* **2007**, *46*, 446. j) C. Knöfel, J. Descarpentries, A. Benzaouia, V. Zeleňák, S. Mornet, P. L. Llewellyn, V. Hornebecq, *Microporous Mesoporous Mater.* **2007**, *99*, 79.

3 S. S. Kim, A. Karkamkar, T. J. Pinnavaia, M. Kruk, M. Jaroniec, *J. Phys. Chem. B* **2001**, *105*, 7663.

4 Supporting Information is available electronically on the CSJ-Journal web site, http://www.csj.jp/journals/chem-lett/index.html. The adsorption capacity of zeolite 13X in the presence of water vapor was very low (0.11 mmol·g^{-1}).

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